SURFACE AREA MEASUREMENTS OF POROUS MEDIA BY MEANS OF TRANSIENT STATE FLOW

A THESIS

Presented to

the Faculty of the Graduate Division

by

George Prichard Reynolds, Jr.

In Partial Fulfillment

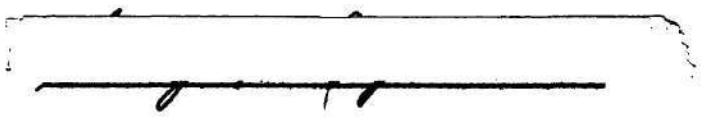
of the Requirements for the Degree

Master of Science in Chemical Engineering

Georgia Institute of Technology

August 1957

"In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.



SURFACE AREA MEASUREMENTS OF POROUS MEDIA BY MEANS OF TRANSIENT STATE FLOW

Approved:

Date Approved by Chairman: Aug 30 57

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. J. M. DallaValle and Dr. Clyde Orr who jointly suggested this problem. The help given by Dr. Orr and his staff who furnished the powders used in these tests is sincerely appreciated.

Mr. C. A. Mayes was of great assistance in the construction of the equipment. Other graduate students in the School of Chemical Engineering offered several helpful suggestions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A, B, c', d, d'	Constants used in solving flow equation
B.E.T.	Braunaur-Emmett-Teller (a method of surface area measurement)
b	Length of packed bed, cm.
C	Concentration, moles/unit volume
D	Diffusion coefficient, $cm.^2/sec.$
d_c	Capillary diameter, microns
K	Gas permeability coefficient, $cm.^2/sec.$
L	Time lag to complete diffusion, sec.
M	Molecular weight of a gas
M.F.P.	Mean free path of a gas, cm. or microns
m	Mean hydraulic radius, cm.
N	Mass flow rate, $gm./cm.^2/sec.$
n	A positive integer
p_1	Inlet pressure to bed, mm. mercury
p_2	Outlet pressure of bed, microns mercury
R	Gas constant, cal./gm. mole/^oK.
r	Capillary radius, cm.
S_v	Surface area, volume basis, $cm.^2/cm.^3$
S_w	Surface area, weight basis, $cm.^2/gm.$
T	Absolute temperature, ^oKelvin
t	Time, sec.
x	Distance, cm.

ε	Porosity or void fraction, dimensionless
λ	Mean free path of a gas, cm. or microns
ρ_b	Bulk density, gm./cm.^{3}
ρ_p	Particle density, gm./cm.^{3}

SUMMARY

The purpose of this work was to construct and test a low pressure, low flow piece of equipment which could be used to measure the surface area of finely divided particles and give results comparable to those found using the accepted methods of nitrogen adsorption and direct microscopic measurement. A transient state flow process involving molecular streaming was to be employed. The device employed consisted of a small tube packed with particles whose surface area is to be determined, and through which a suitable gas is made to flow at very low pressures.

The earliest work concerning molecular streaming was carried out by Knudsen (1) who passed various gases through capillary tubes of different diameters at low pressures. To obtain so-called Knudsen flow the system under consideration was operated in a vacuum up to five microns mercury where, considering the fineness of the particles used, a mean free path of the gas many times that of the capillary diameter was obtained.

Determination of certain physical properties of a packed bed depends on the time it takes for a gas to diffuse the length of the porous material. Calculation of the diffusion coefficient follows from the use of Fick's second law after solution using Fourier series. The capillary

radius and surface area of the particles may then be determined.

In the system built for the present work a diffusion pump was used to decrease pumpdown time, and a thermocouple vacuum gauge was employed to measure pressures. The remaining apparatus consisted of two steel tanks, high vacuum valves, and necessary interconnecting copper tubing. The volume totaled about 488 cubic inches. An 11 cm. brass tube with flanged ends was designed to serve as a bed holder for the porous materials. O-ring gaskets were used to seal the removable bed holder while the remainder of the connections were soldered or threaded. The assembled system was mounted in a compact cabinet 18 X 24 X 12 inches.

To test the apparatus, surface area determinations were made of eight different materials with particle sizes ranging from 70 to 0.02 microns. Surface areas obtained ranged from 0.19 to 57 square meters per gram. Most of the results gave reasonable checks on measurements made using the Braunaur-Emmett-Teller method. However, increasingly lower results were obtained for materials having larger surfaces. If it is desired to measure particles larger than 10 microns with any accuracy a longer bed tube is recommended.

CHAPTER I

INTRODUCTION

The use of porous and particulate media occupies an important place in the field of chemical engineering. Many of the unit operations employ packings. The most important property of packings thus employed is the amount of surface provided for mass separations such as distillation, filtration, adsorption and extraction, or for promotion of reactions where they serve as catalysts. Other applications affected by surface area are setting properties of cement, rate of combustion of solid rocket propellants, and sintered metal compacts. This report deals with the measurement of the surface area of a particular type of non-consolidated porous media--fine particles or powders.

There are several common methods for measuring the surface area of the type material just mentioned. The best known is perhaps the Braunauer-Emmett-Teller method of nitrogen adsorption--a non-flow process. The present investigation arose from the desire to have available a device which could provide a more rapid and possibly a more simple means of obtaining surface areas of fine powders than the methods commonly used. In recent years flow procedures involving either viscous, "slip" or Knudsen flow of gases through porous media have come into use. This investigation involved the problem of

building and testing a device which could be used to measure surface areas utilizing Knudsen flow. It was hoped to obtain results comparable to those found using the accepted methods of nitrogen adsorption and direct microscopic measurement.

Description and Utilization of Knudsen Flow.--Viscous flow of gases through solids occurs when the diameters of the pores of the media are much larger than the mean free path (M.F.P.) of the gas. Thus viscosity of the gas actually retards the flow. Slip flow exists when the mean free path is approximately equal the pore diameter, and Knudsen flow is obtained when the mean free path is many times larger than the pore diameter. In order to utilize Knudsen flow the pore spaces in a porous bed are considered as analogous to a bundle of capillaries. Thus, Knudsen flow implies molecular streaming since the ratio of mean free path to capillary diameter is large. This large ratio may be achieved by either or both of two means: (1) use of ultra fine particles to achieve small pores, and (2) adjustment of the properties of the gas passing through the bed--in particular its pressure--to increase the mean free path. Table 1 is a typical example presented to illustrate the above cases.

Table 1. Effect of Capillary Diameter and Mean Free Path toward Achieving Knudsen Flow.

Material	Pore Diameter, microns	Pressure, mm.mercury	M.F.P.[a] Air, microns	M.F.P.[b] Helium, microns	Ratio of M.F.P. to pore Diameter	
					Air	Helium
Mapico Red[c]	0.08	760	0.06	0.18	0.75	2.3
Mapico Red	0.08	100	0.46	1.37	5.8	72.5
Sand	67	760	0.06	0.18	0.0009	0.0027
Sand	67	0.05	920	2700	14	40

It is seen that for very fine materials such as paint pigments, conditions for Knudsen flow could exist almost at atmospheric conditions. For larger particles (sand having these pore dimensions would be about 30 to 40 mesh,) the flow would have to take place in a high vacuum to increase the ratio of mean free path to pore diameter. Use of the lighter gases also increases the mean free path.

Equations have been developed for utilizing Knudsen flow by likening it to a diffusion process. Barrer (3,5,6) has been one of the leaders in this work. In diffusion it is assumed that the resistance to the movement of a gas due to viscosity can be neglected and that the gas moves very slowly. This is essentially true for a tightly packed bed of fine particles

[a]Reference (2).

[b]Reference (3).

[c]Reference (4).

through which a gas can penetrate only over some period of time. By reducing the pressure to achieve Knudsen flow the gas is spread out so that viscosity is negligible. The molecules collide only with the capillary walls and not with one another.

Two states of diffusional flow are possible--the steady and the non-steady states. Where transient state flow exists Fick's second law of diffusion is utilized.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

Experimental conditions can be fixed so that the above equation applies. It is linear and capable of explicit solution. A porous bed of material is evacuated, using a vacuum pump, to a pressure or gas concentration of practically zero. This concentration will exist until a gas passing through the bed has diffused the total bed length, b. The gas concentration on the high pressure side will be constant at C_o. The boundary conditions for (1) are then as follows:

$C = C_o$ at $x = 0$ for all t.

$C = 0$ at $x = x$ for $t = 0$.

$C = 0$ (approximate) at $x = b$ for all t.

The solution to the above has been indicated briefly in the Appendix for later reference. The end result of (1) is used with Fick's first law,

$$N = -D\frac{\partial C}{\partial x} \qquad (2)$$

to determine the total amount of gas which has diffused through the bed at any time. The time lag, L, which occurs before any gas travels the total length of packing, b, is given by

$$L = \frac{b^2}{6D} \qquad (3)$$

A plot of time against pressure of the gas emerging from the bed (since pressure is directly proportional to concentration at low pressures) permits evaluation of the time lag. The accepted procedure is to extrapolate the steady state portion of the curve back to the original bed pressure at the start of the run. The diffusion coefficient may then be calculated.

Previous Work.--As mentioned, Knudsen (1,3,7,8,9) was the first to study the effect of the "molecular streaming" type flow which received his name. He passed different gases through capillaries and varied the mean free path from 3000 to 0.00222 times the capillary diameter. When this ratio was about 10 he found the flow rate became independent of the mean pressure (9).

Other investigators have utilized Knudsen flow for various purposes. Barrer, an originator of the time lag method, and Grove (4) studied the flow of 10 different gases through beds of analcite crystals.[1] They used a transient

---

[1]These particles are similar to small glass beads. Their average diameter was 50 microns.

state of flow in beds 98 cm. long and obtained time lags up to 100 minutes. Values were much less for the lighter gases used, however.

Kraus et al. (10) compared the method under consideration with steady state flow and non-flow methods and obtained good checks. They calculated the surface areas of five powders using bed lengths up to 60 cm. and glassware equipment. Carmen (7), however, has refused to accept some of Kraus' other work since he believed the latter was not actually obtaining Knudsen flow.

Carmen (11) has investigated the kinetics of adsorption of porous media by diffusing n-butane at - 10°C. into a porous plug of Linde silica. Transient state flow methods were found to give the same results as the steady state except when the plug was nearly saturated.

Quite recently much interest has arisen concerning molecular streaming which occurs during supersonic flight (9). "At altitudes above 100 miles the mean free path may be appreciably larger than the over-all dimensions of the aircraft."[1] Thus Knudsen flow at high velocities may be of great importance in years to come.

Adaption of Time Lag to Surface Area Calculations.--The method employed by Kraus et al. (10) has been followed in calculating surface areas. They used the equation developed by Derjaguin

---

[1]Patterson, G. N., Molecular Flow of Gases, New York: John Wiley & Sons, Inc., (1956), 159.

(7) who applied a statistical method to follow the motion of a free molecule through a random pore space. Thus Derjaguin eliminated the somewhat arbitrary tortuosity factor and arrived at the following relation for the permeability coefficient:

$$K = \frac{12}{13} \varepsilon m V \tag{4}$$

The relation from kinetic theory (12) for the mean thermal molecular velocity,

$$V = \sqrt{\frac{8RT}{\pi M}} \tag{5}$$

the expression for mean hydraulic radius (3),

$$m = \frac{1}{S_v} \frac{\varepsilon}{1-\varepsilon} \tag{6}$$

and the relation between K and the effective diffusion coefficient (7),

$$K = \varepsilon D, \tag{7}$$

are substituted in (4) to obtain

$$D = \frac{24}{13} \frac{\varepsilon}{1-\varepsilon} \frac{1}{S_v} \sqrt{\frac{2RT}{\pi M}} \tag{8}$$

Inserting the time lag relation for D from (3) and rearranging gives the final equation used to calculate surface areas.

$$S_v = \frac{144}{13} \frac{\varepsilon}{1-\varepsilon} \frac{L}{b^2} \sqrt{\frac{2RT}{\pi M}} \tag{9}$$

In using (9) the following conditions have been assumed

and must be met for this equation to apply:

1. The resistance to flow is due only to collisions of the gas with the capillary walls, i.e. diffusion applies.
2. The boundary conditions previously listed apply.
3. The porosity of the bed is constant along the length of the packing.
4. Isothermal flow exists.
5. The gas is ideal.

These assumptions were closely approximated in actual practice and are discussed in more detail in Chapter IV.

Object of the Present Work.--Briefly, the objectives of the present investigation were to construct a permanent apparatus of metal and to improve on the techniques used in previous studies. It was desired to discover how close surface areas found by this method would compare with B.E.T. and other surface areas. A short bed holder was to be used in the system. This was expected to result in shorter operational periods due to decreased pumpdown time and shorter time lags. Ease of packing the bed and the liklihood of obtaining a constant porosity would be increased. To test the system a wide range of particle sizes and shapes was to be used. The effect, if any, of initial bed pressures and pressures at the bed inlet was to be determined. Results were then to be compared with known surface areas obtained by other methods.

CHAPTER II

INSTRUMENTATION, EQUIPMENT, AND MATERIALS

Apparatus

The apparatus consisted of the following component parts whose relationship is shown by the flow sheet of Figure 1.

Volume Reservoirs.--Two cylindrical tanks were made from a nine inch section of six inch diameter steel pipe. The top and bottom sections were made by cutting a six inch circular piece from one-quarter inch steel plate and trimming on a lathe until smooth. A tight seal was obtained by shrink fitting the circular ends into the cylinder and brazing around the seam. Any pinholes which appeared were soldered, since the higher temperature required to seal them by rebrazing would open the seam at some other point. Two three-eighths inch holes were drilled in the tops for tubing and vacuum tube connections. The tanks were painted with aluminum paint to prevent rusting. Each had a volume of 241 cubic inches.

High Vacuum Valves and Interconnecting Tubing.--Block valves in the system were Hoke toggle valves (450 series) made of brass. The valve bodies were forged, and the synthetic rubber seats were spring closing. They had previously been leak tested with helium to insure satisfactory high vacuum operation. The inlet and outlet of the valves had three-

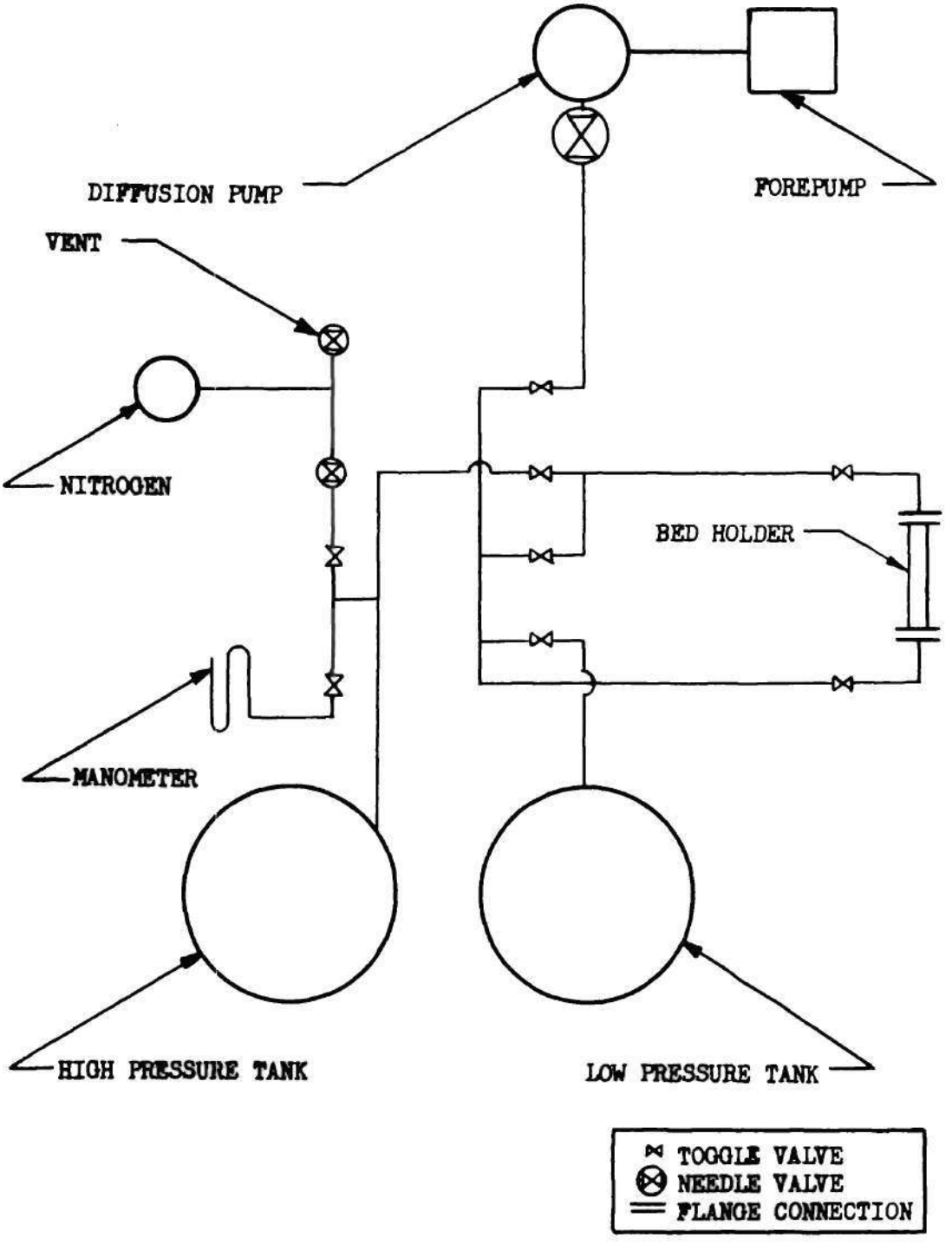


Figure 1. Schematic Flow Sheet of Apparatus with Valves Shown in Panel Board Position

eighths inch NPT male threads. The necessary interconnecting lines were cut from three-eighths inch copper tubing. Connections were made by soldering the tubing into a special tube fitting which was pulled snugly into an inlet or outlet socket of a valve by a nut screwed onto the valve thread. A Hoke bar stock needle valve, also brass, was provided for close flow control when filling the tank on the inlet side of the packed bed with gas. A vent valve was also provided to air release the system.

Bed Holder.--The five inch brass tube which has an 11/32 inch diameter opening and is pictured in Figure 2, was constructed to hold the material being tested. The flanged connections, fitted with one inch O-rings, gave a good seal and one that could be quickly broken when the porous packing was ready to be changed. The plunger, shown also in Figure 2, was used to pack the powder into the tube. Perforated brass plates backed by filter paper were used to contain the packing in the bed. A heater made of a nine inch section of Briskheat[1] connected to a variac was provided to wrap around the bed holder and aid in outgassing the porous materials. Thus pumpdown time was greatly reduced for powders having large surface areas.

Vacuum Gauge.--A Hastings thermocouple vacuum gauge (model

---

[1]Briskheat is a strand of nickle-iron alloy wire covered with glass fibers and woven into a half inch band.

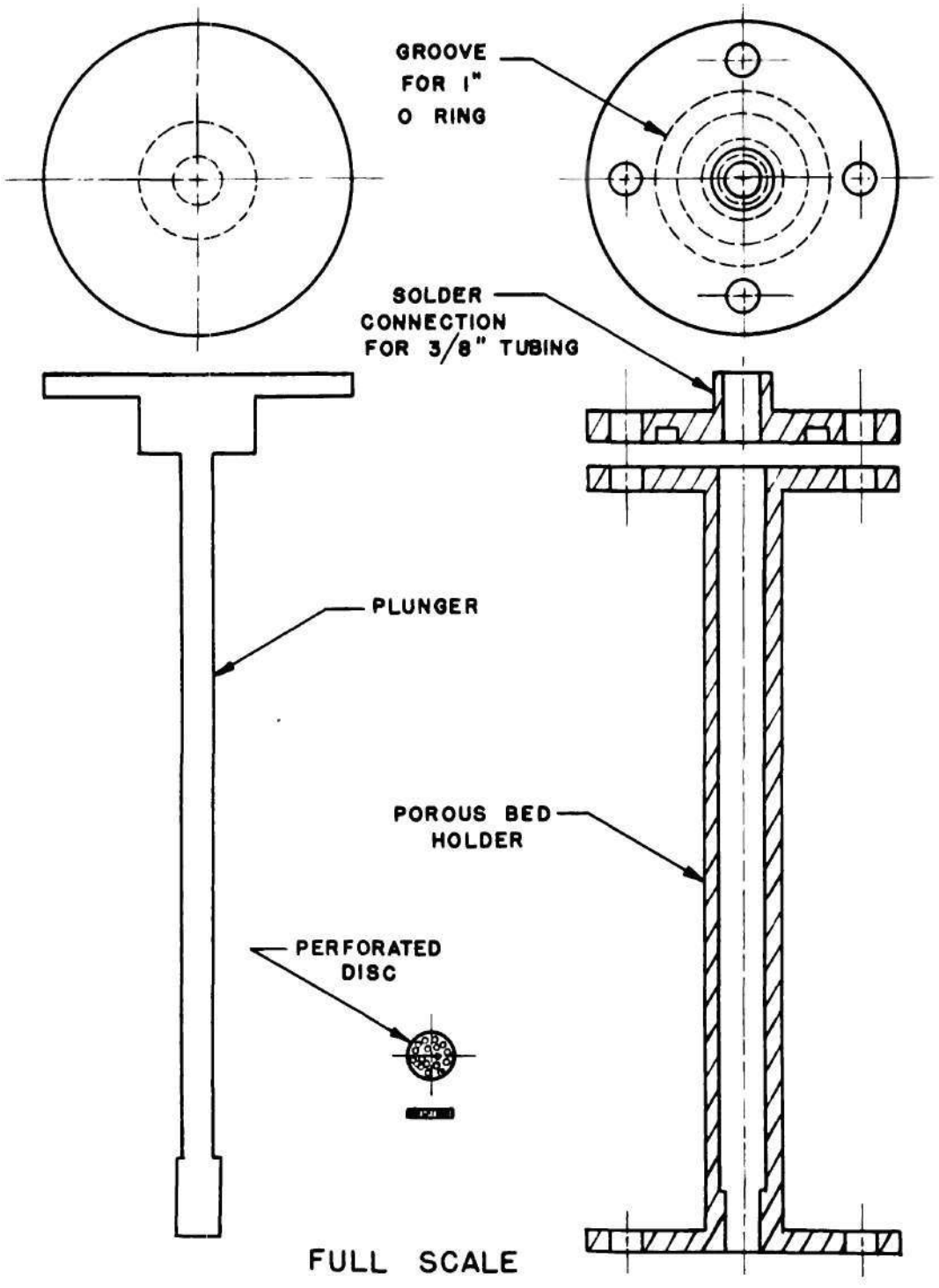


Figure 2. Packed Bed Assembly

GV-3) having a range of 1-1000 microns of mercury was used to measure pressures below one millimeter. The gauge tubes were provided with one-eighth inch IPS male threads. They were coupled to the vacuum source by a threaded hole in the top of each tank. The gauge itself is a portable type and was arranged in the panel so it could be removed and replaced easily if desired. The original thought in providing the high pressure tank with a measuring station was that the inlet bed pressure would be on the order of one millimeter mercury for very fine powders. However, in actual practice from five to 20 millimeters were used. A six inch mercury manometer was provided to measure this pressure.

Pumps.--The system was equipped with two pumps. The forepump was a Welch duo seal vacuum pump of one-third horsepower. The diffusion pump was a two inch National Research Corporation model. Both dibutyl phthalate and di-2-ethylhexyl phthalate were tried as pumping fluids. The former, having a higher vapor pressure (200 microns mercury at 120°C.), seemed to be better over the pressure range employed. However, it is doubtful that either of these liquids would be as efficient as Narcoil-10, the fluid which is recommended for this particular pump.

The inlet connection to the diffusion pump was made vacuum tight by sealing the flanged line to the lip of the pump's cylindrical body with De Khotinsky cement. A section of rubber vacuum hose connected the forepump to the diffusion pump.

When assembled, the apparatus was mounted in a compact

case having a panel one and one-half by two feet in size. A view of the panel is shown in Figure 3. Figure 4 is a rear view of the cabinet showing tanks, valves, and tubing. Before testing the apparatus a leak check was made and pinholes closed using Fisher pyseal cement. The O-rings on the bed holder gave very little trouble. The soldered joints were also good seals.

Auxiliary Equipment

A precision balance for weighing the porous materials, a Secron timer to measure time lags, a Centigrade thermometer for obtaining room temperatures, a laboratory type oven for drying the powders, pycnometers, a thermally regulated water bath and a cylinder of dry nitrogen complete the equipment used in this work.

Porous Bed Materials

All powders used in testing the apparatus were obtained from the Micromeritics laboratory at Georgia Tech. Eight materials, including three sizes of glass beads and two of silica, were used. Particle diameters ranged from 70 microns to a few hundredths of a micron. Particle shapes included spherical, hexagonal, and plate. Typical powders are pictured in Figures 5 and 6. Table 2 lists the powders and some of their properties.

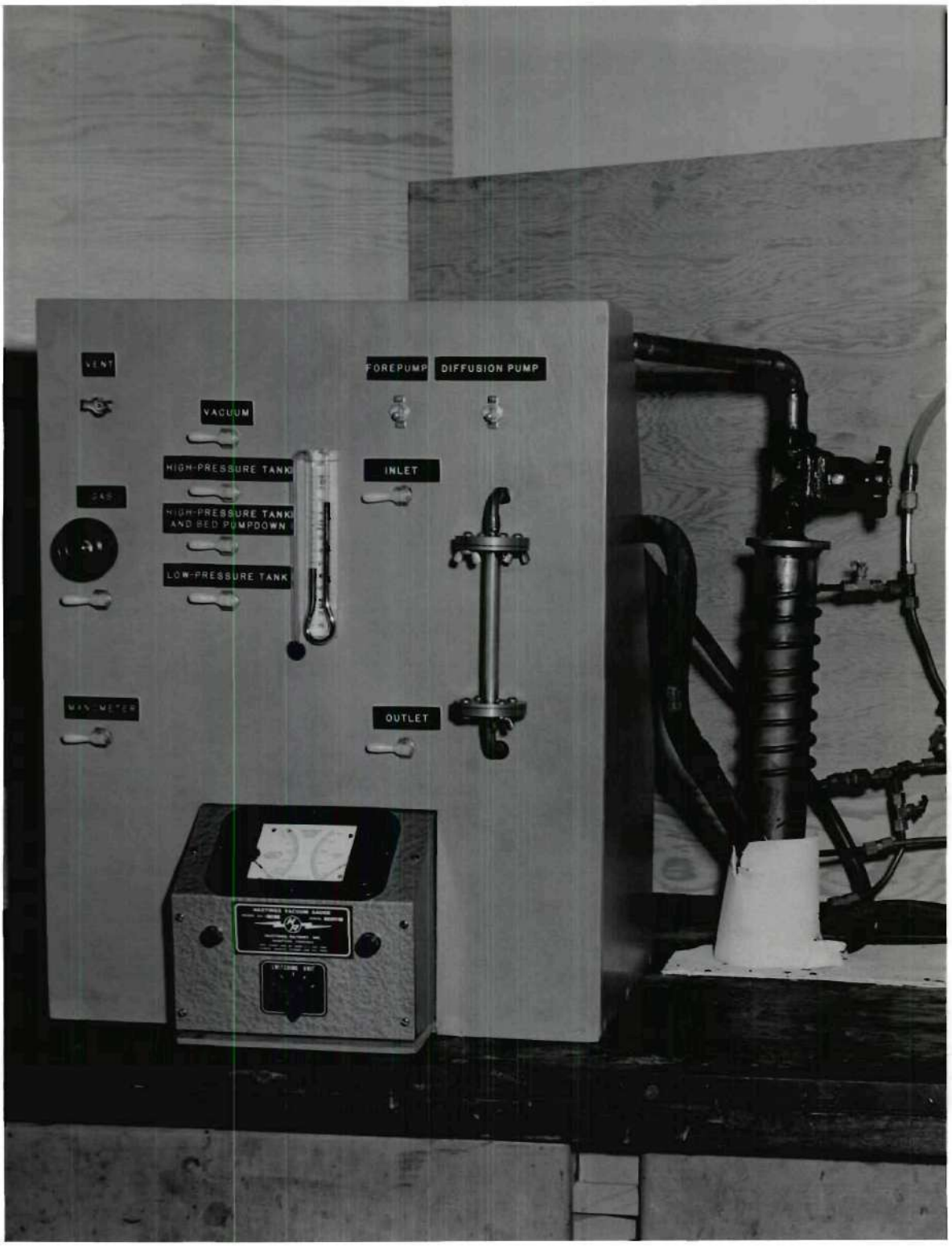


Figure 3. Assembled Apparatus

Figure 4. Rear View of Cabinet Showing Tanks, Valves, and Tubing

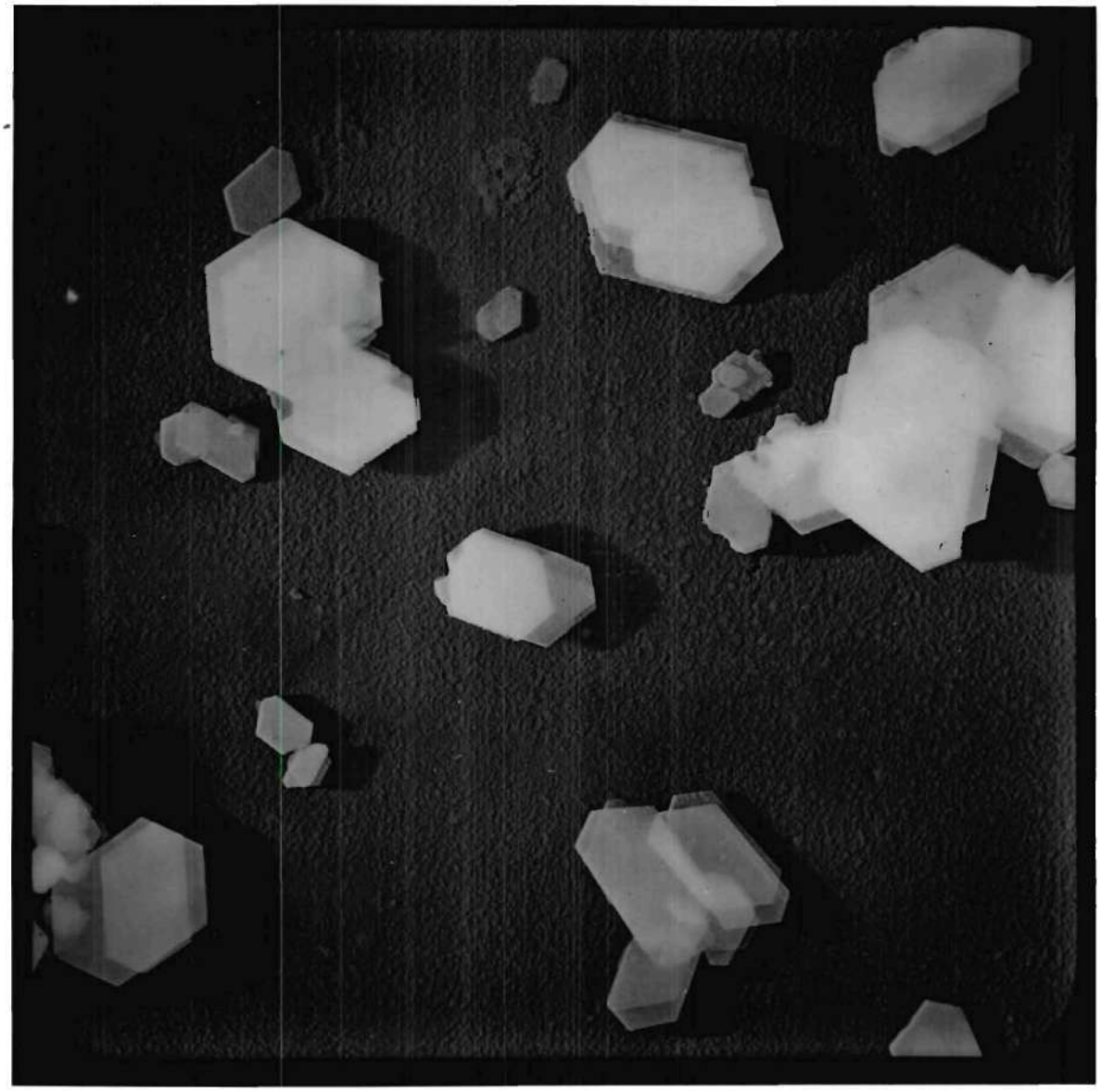


Figure 5. Plate Shaped Kaolin Particles at 25,000 X on a Colloidal Film Background.

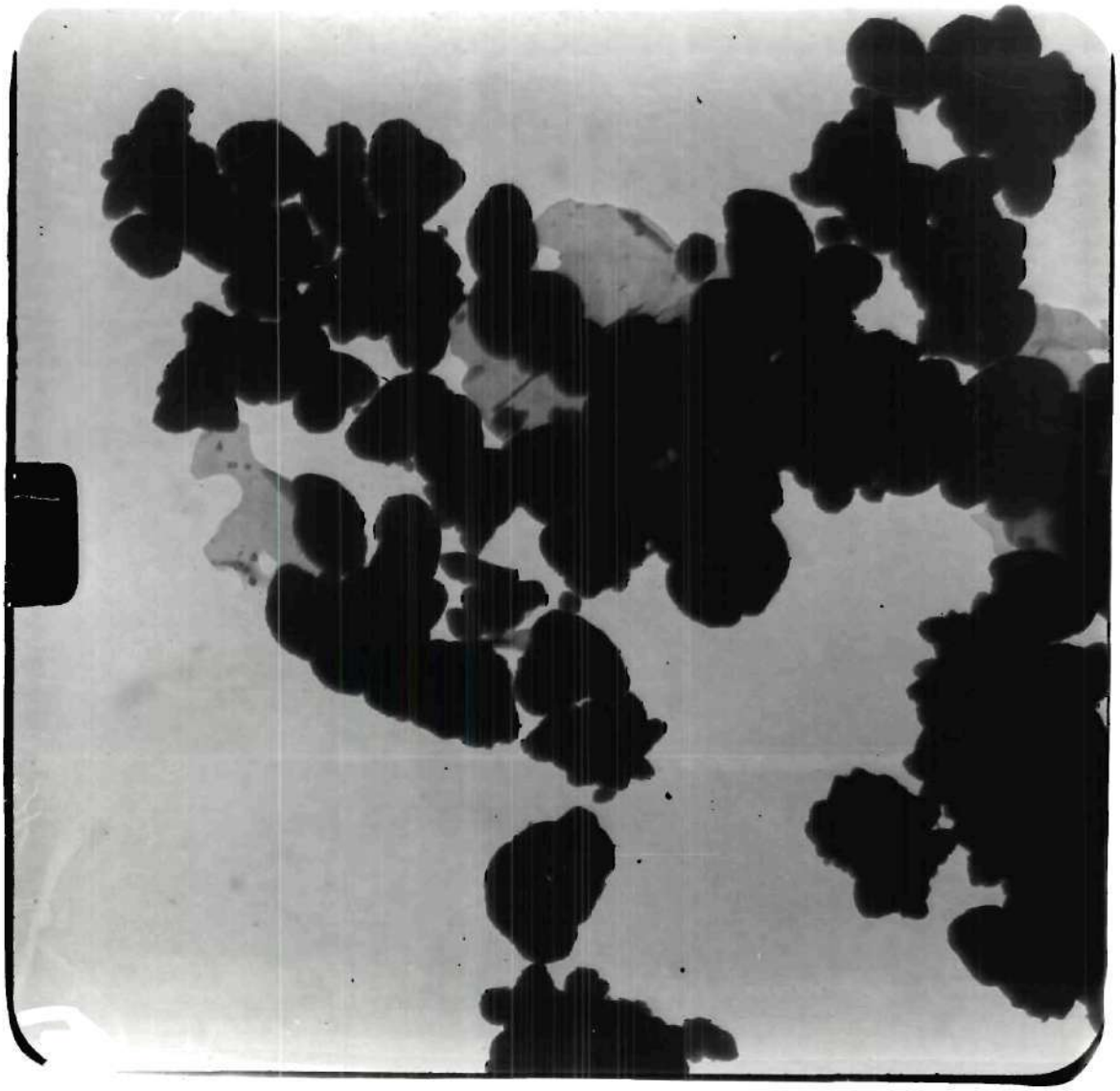


Figure 6. Iron Oxide Particles at 27,000 X

Table 2. Properties of Powders

Material	Particle Size,[1] microns	Particle Shape	Specific Gravity
Glass Beads	70	Spherical	2.44
Glass Beads	36	Spherical	2.44
Glass Beads	28	Spherical	2.44
Silicon Carbide	3	cubic	3.17
Aluminum Oxide	0.65	trigonal	4.00
Iron Oxide	0.26	Hexagonal	5.12
Kaolin	0.047	Plate	2.6
Silicon Dioxide I	0.036	cubic-rhombic	2.2
Silicon Dioxide II	0.017	cubic-rhombic	2.2
Clay I	0.008	irregular	2.58
Clay II	0.24	irregular	2.58
Cupric Oxide	0.40	Cubic	6.40

[1]With the exception of the glass beads and silicon carbide these values are based on the B.E.T. surface area. See Appendix II. The exceptions are microscopically obtained values.

CHAPTER III

PROCEDURE

Density Determinations.--Particle density is needed to calculate the bed porosity of a packing as well as to express surface as area per unit weight. With the exception of the glass beads the specific gravity of the materials used was obtained from handbooks.[1] Density of the glass beads was checked by the pycnometric method. (13) The immersion liquid was distilled water. Outgassing of the trapped air was achieved by boiling the liquid under a vacuum pulled by an aspirator.

Preparation of the Porous Bed.--The powder to be used was first dried in an oven at 140° Centigrade for several hours. The porous bed was prepared by adding small and approximately equal amounts of powder to the bed holder. As each portion of material was added it was packed into place using the brass plunger. Weights up to two kilograms, which applied as much as 50 pounds per square inch to the packing, were placed on the plunger flange while packing the bed. By using the same weights, porosities could be reproduced within less than ten per cent for a given material.

---

[1] Chemical Engineers' Handbook, John H. Perry, ed., New York: McGraw-Hill Book Co., 1950. Handbook of Chemistry and Physics, C. D. Hodgman, ed., Cleveland, Ohio: Chemical Rubber Publishing Co., 1953, 35th edition.

A perforated plate with a piece of filter paper to the inside was placed at each end of the packing to prevent loss of material during the run. The bed holder was weighed before and after packing to obtain the weight of powder. The packed length was found with a centimeter rule.

Preparation of System for a Run.--The bed holder was sealed in the system by placing O-rings on the flanges and securing with bolts and wing nuts. The forepump was started with all valves on the panel, including the vent, open. Dispersion of any powder from the bed by a sudden pressure surge was thus avoided as a small amount of air was bled in from the atmosphere, and the differential across the packing was kept small. When the vacuum reached a few millimeters of mercury the vent and gas valves were closed. The diffusion pump heater was turned on when the pressure reached 500 microns. Adjustment of the heater on the bed to 20 volts heated the tube to about 170°F. which is still low enough not to harm the O-rings. If the high pressure tank has been open to the atmosphere or if some gas other than the one to be used in the run under way was used previously, the tank should be pumped as low as possible. It should then be flushed with the new gas and pumped down again. In the present work cylinder nitrogen was used in each run. Therefore, the high pressure tank was not usually flushed but was only pumped to about 200 microns before adding the gas. This was done by isolating the tank from the pump, opening the gas toggle valve, and controlling the

flow of nitrogen from the cylinder with the needle valve. When the pressure reached several millimeters of mercury the flow of gas was stopped, and the appropriate valves were closed. The exact pressure to be fixed in the tank depended on the particle size used. A lower pressure was necessary to achieve Knudsen flow with larger particles, and a higher pressure was needed to give a greater driving force to provide a suitable pressure-time curve for very fine materials. If the particle size is unknown the pressure to use is best found by trial.

The low pressure tank and the bed were always evacuated to as low a pressure as possible. (five to ten microns). The system was valved off from the pumps, and the valve marked "high pressure tank-bed" was closed. This valve allowed one to pump down the high pressure tank, the bed, or both. By opening the valve to the high pressure tank, nitrogen was then allowed to flow through the bed forcing out any trapped gas. After a 10 or 20 micron pressure rise in the low tank the high tank valve was closed, and the low pressure tank again pumped to as low a pressure as possible.

Measurement of Time Lag.--The same valving procedure was again followed to start gas flowing when beginning an actual run. At the time the high tank valve was opened the pressure in the low tank was noted and a timer started. Low tank pressure readings were recorded every ten seconds for the first minute and every 15 or 30 seconds thereafter until the run was

complete as noted by attainment of steady state flow for about three minutes.

Pressure (ordinate) was plotted versus time (abscissa). The straight line portion of the curve was extrapolated to the initial pressure and the time at that point taken as the time lag, L. Figures 7 and 8 are typical plots showing a long and a short time lag at different inlet pressures for two of the materials used. Other time lag plots are similar and have not been included in the thesis. Instead values of the time lags are tabulated in the Appendix, Table 5.

After the initial run the bed and low pressure tank were again pumped down and the entire procedure repeated until at least three consistent time lags were obtained. Pressures in the high pressure tank were often varied to note any effect on the resulting time lag.

When a set of runs was completed the vacuum in the low tank could be maintained by "valving" it off. The bed and high tank were then vented, the bed holder removed and a new packing prepared. On the next run the low tank could be "valved" in when the high tank and bed reached the low tank pressure. At all times care must be exercised not to open the bed to a lower pressure, thus throwing powder into the valves and pumping system.

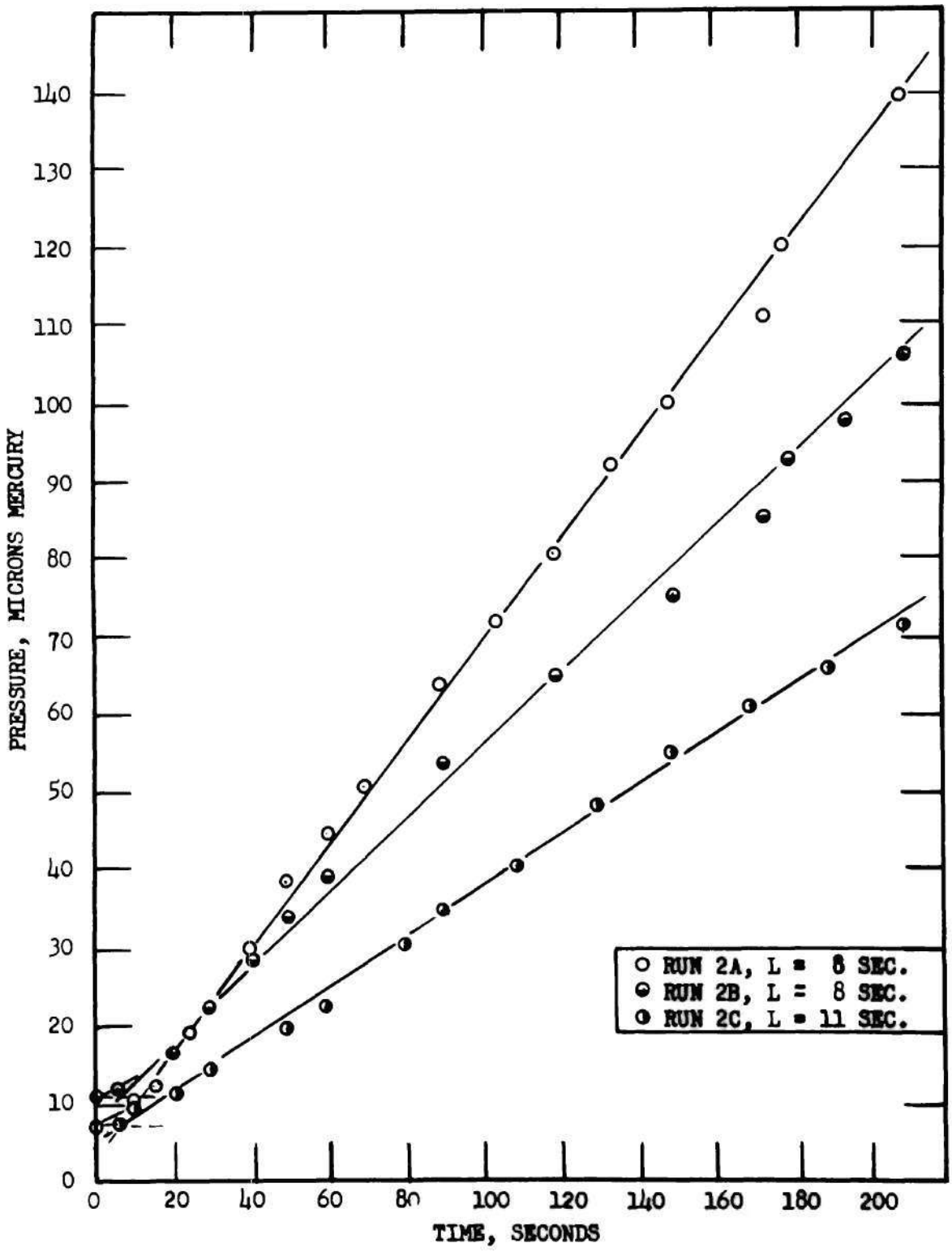


Figure 7. Time Lag Plots for 36 Micron Glass Beads

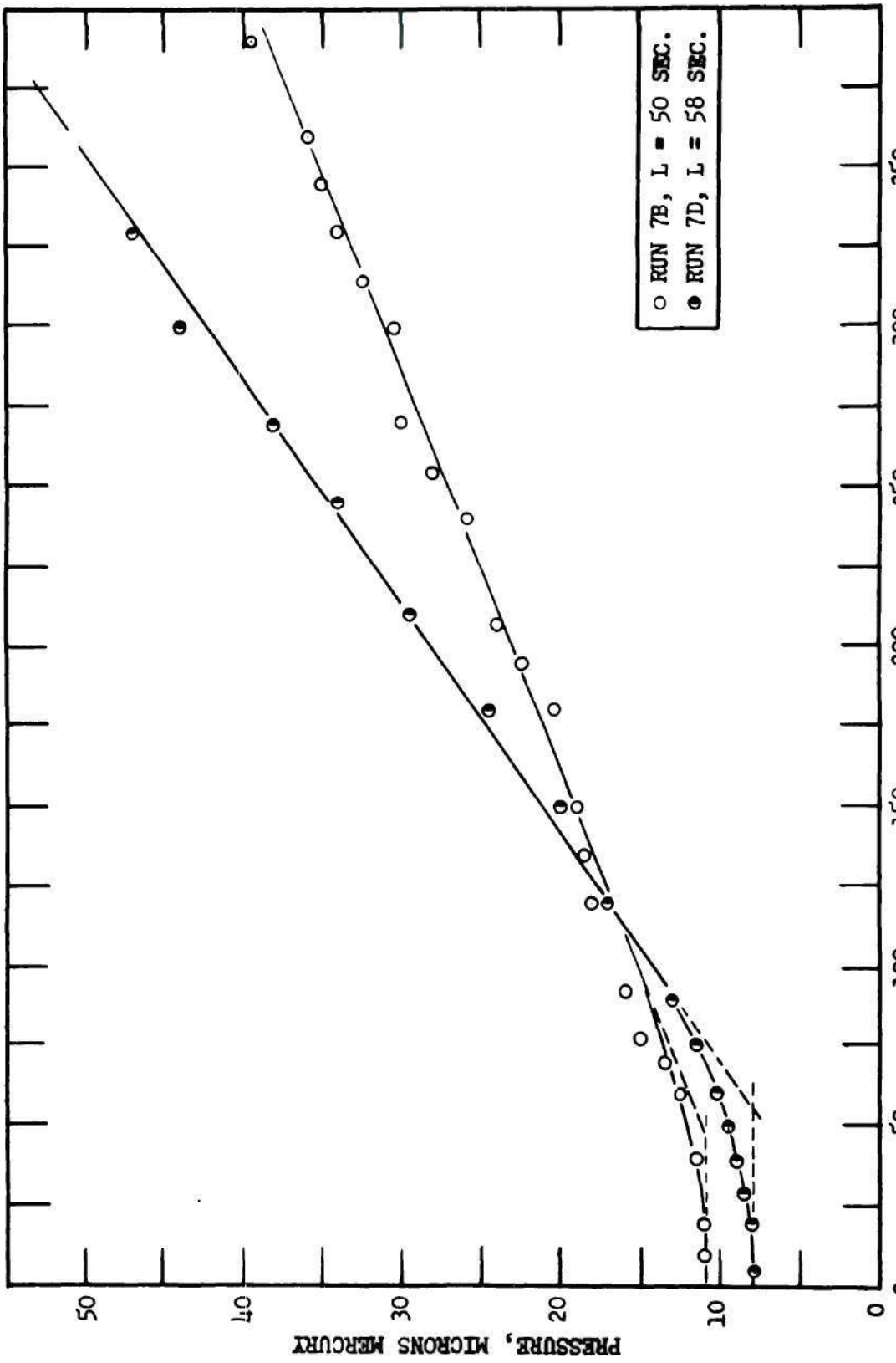


Figure 8. Time Lag Plots for Iron Oxide Particles

CHAPTER IV

RESULTS AND DISCUSSION

The results obtained from tests performed on the equipment are summarized in Table 3 and compared with surface areas obtained by other methods. Data for these runs are given in Appendix, Table 5.

Table 3. Comparison of Surface Area Values

Material	Surface Area	
	Time Lag M.^{2}/gm.	Other M.^{2}/gm.
70 micron Glass Beads	0.19	0.035[a]
36 micron Glass Beads	0.57	0.068[a]
28 micron Glass Beads	0.80	0.088[a]
Silicon Carbide	0.68	
Aluminum Oxide	2.55	2.29[b]
Iron Oxide	5.34	4.2 [b]
Iron Oxide	5.45	4.2 [b]
Kaolin	43.8	48.7[b]
Silica I	57	88 [b]
Silica I	48	88 [b]
Silica II	55	186 [b]
Clay I	56	280 [b]
Clay II	10.1	9.56[b]
Cupric Oxide	2.12	2.36[b]

[a]Value is based on diameter measurements.

[b]Value is based on B.E.T. measurements.

Agreement with accepted values can be termed fair with the exception of the powders having very high surface areas. Apparently the time lag method does not hold true for materials with areas larger than 50. Carmen (7) has stated that he would not expect a flow process to give as high an area as a non-flow method. Certainly, results will be low for materials whose particles are themselves porous, which is possible for the clay and silica. Although the glass beads have much larger areas than the statistical calculation would indicate it is probable that they would compare favorably with a B.E.T. value were it available.

From Table 5 in the Appendix inspection reveals that the inlet bed pressure, P_1, appears to have little effect on the time lag, L, within limits of experimental error. This was also true of the initial bed pressure, P_o. Of course P_o should be low to satisfy boundary conditions of the flow equation and insure Knudsen flow. Ratios of mean free path to capillary diameter, shown in Table 7, were calculated to determine if Knudsen flow conditions were being met. It is seen that some of the ratios are rather low on the inlet side of the bed. However, at other inlet pressures for the same material there is little deviation in the time lag obtained. It is probable that the pressure drop over a small section of packing is very large. Thus P_1 would be reduced greatly a short distance down the packed bed. The ratio $\frac{M.F.P.}{d}$ would then increase, resulting in Knudsen flow.

The following paragraph considers the experimental error of the variables in these tests:

Densities of the particles should be accurate to within 1.0 per cent, with the exception of the silica and kaolin whose crystalline form was uncertain. The values used for these particles may be as much as 10 per cent in error. If the accuracy of the weight and volume measurements are considered, porosities are good to within 2.0 per cent. At least three time lags were used to obtain an average for any given sample. The maximum deviation from the average was about 10 per cent. Temperatures for a series of runs varied as much as 3°C. The temperature used in calculating a surface area for a given average time lag was the average temperature of each run for a respective sample. This resulted in a possible deviation of 0.2 per cent in the value of the square root of the absolute temperature used in the surface area calculation. The possible error then for a given surface area calculation is about 15 per cent when all the factors just mentioned are considered.

The largest responsible factor of error is obviously the value for the time lag. For the larger particles tested L was small and consequently any error made in the lag measurement resulted in a large error percentagewise. For all of the runs a major difficulty lay in the fact that the pressure rise often did not become perfectly linear as expected. Thus the straight line drawn for extrapolation to the

original pressure could be placed somewhat arbitrarily, and it was difficult to determine L with great accuracy. Some of the scattering of points on the time lag plot can be attributed to the thermocouple gauge which was very sensitive to current setting and which tended to drift. It was necessary constantly to adjust the current set during a run.

CHAPTER V

CONCLUSIONS

The conclusions resulting from this work are summarized as follows:

1. A Knudsen flow type of apparatus may be used to determine surface areas of non porous powders except for materials having areas larger than about 50 $M.^2/gm.$

2. Powders of about 10 micron diameter particle size are the largest that can be accurately measured with the bed holder provided; a longer holder would be required for larger particles.

3. The pressure on the inlet side of the bed is not critical but should give a pressure rise slow enough to measure and rapid enough to provide a proper time lag plot.

4. The initial bed pressure should be low enough to insure Knudsen flow and preferably should be as low as possible.

5. This method is more rapid than the B.E.T. method, but is best suited for product control after suitable checking with the letter.

6. The accuracy of the technique depends on establishing true Knudsen flow through a packing and on the rapidity with which equilibrium is achieved point-wise as flow proceeds through the packing.

CHAPTER VI

RECOMMENDATIONS

To improve the accuracy and efficiency of the apparatus the following recommendations are submitted:

1. A longer bed should be constructed if it is desired to obtain more accurate measurements with powders larger than 10 microns.

2. Gases other than nitrogen should be investigated as a flow medium.

APPENDIX

APPENDIX I

SOLUTION OF FLOW EQUATION (6, 15)

Fick's second law is to be solved using the indicated boundary conditions.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

$$f(0,t) = C_o \qquad (I)$$

$$f(x,0) = 0 \qquad (II)$$

$$f(b,t) = 0 \qquad (III)$$

The usual procedure is to assume a product solution so that:

$$d = \text{a constant} = X(x) \cdot T(t) \qquad (10)$$

D is assumed constant since the equation will apply over a very narrow concentration range. Proceeding in the general manner and using (1) and (10) two solutions are obtained:

$$C = d'x + c' \qquad (11)$$

and,

$$C = (A\cos\lambda x + B\sin\lambda x)\, e^{-\lambda^2 Dt} \qquad (12)$$

In the above equations A, B, λ, d', and c' are constants which must conform to the boundary conditions. Application of conditions (I) and (III) to (11) gives

$$C = C_o \left(1-\frac{x}{b}\right). \tag{13}$$

This is one particular solution which reduces to zero when $x = b$, and the others are required to do the same.

Substitution of II into (12) gives

$$0 = A\cos\lambda x + B\sin\lambda x. \tag{14}$$

For (14) to hold true, since A and B both cannot be zero, A is assumed to be zero and thus

$$\lambda = \frac{n\pi}{b} \tag{15}$$

Now for (12) the infinite set of particular solutions,

$$C_n = B_n \sin\frac{(\pi_n x)}{(b)} e^{-\lambda^2 Dt}, \tag{16}$$

to which the other particular solution, (13), is added to obtain

$$C(x,t) = C_o\left(1-\frac{x}{b}\right) + \sum_{n=1}^{n=\infty} B_n \sin\frac{n\pi x}{b} e^{-\lambda^2 Dt} \tag{17}$$

After applying boundary condition (II) to (17) B_n is evaluated using Euler's half range sine expansion.

$$B_n = \frac{2}{b}\int_0^b C_o\left(\frac{x}{b} - 1\right)\sin\frac{n\pi x}{b}\, dx \tag{18}$$

$$= \frac{-2C_o}{n\pi} \tag{19}$$

Substitution into (17) gives

$$C(x,t) = C_o(1-\frac{x}{b}) \quad \frac{2C_o}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi x}{b} \, e^{\frac{-n^2\pi^2 Dt}{b^2}} \qquad (20)$$

According to Fick's first law the total amount of gas which has diffused after time t per unit cross section is:

$$N = -\int_0^t D \frac{\partial C}{\partial x} \, dt \qquad (21)$$

After performing the indicated differentiation of (20) and substituting the result into (21) integration yields:

$$N = \frac{C_o D}{b}\left[t - \frac{2b^2}{\pi^2 D} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \cos \frac{n\pi x}{b} \left(e^{\frac{-Dn^2\pi^2 t}{b^2}} - 1 \right) \right] \qquad (22)$$

At the end of the bed x equals b. Substitution into (22) gives

$$N = \frac{C_o D}{b} \left(t - \frac{b^2}{6D} \right) \qquad (23)$$

Since $\frac{(-1)^N}{N^2} = -\frac{\pi^2}{12}$, and the other term converges to zero.

However, no gas has diffused the total length b until adsorption is complete. At that instant N is still zero. Therefore the time lag of the gas to travel

distance b is

$$t = L = \frac{b^2}{6D} . \qquad (3)$$

APPENDIX II

SAMPLE CALCULATIONS

The pycnometric density calculations are based on the first sample listed in Table 4. The other calculations are based on Run No. 7 (iron oxide). Data are from Table 5; densities are from Table 2.

Pycnometric Density.--See Table 4. At 30.2°C. the density of water is 0.9956.

$$\text{volume of water} \quad \frac{19.1648 \text{ gm.}}{0.9956 \ \frac{\text{gm.}}{\text{cm.}^3}} = 19.2491 \text{ cm.}^3$$

$$\text{volume of powder} \quad 23.4075 - 19.2491 = 4.1584 \text{ cm.}^3$$

$$\text{density of powder} \quad \frac{10.1890 \text{ gm.}}{4.1584 \ \text{cm.}^3} = 2.45 \ \frac{\text{gm}}{\text{cm.}^3}$$

Porosity.--See Table 6.

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} = 1 - \frac{\text{Weight of particles in bed}}{\text{Volume of bed} \times \rho_p} \qquad (24)$$

Where bed volume = bed cross section x length

$$= \frac{\pi}{4} \left(\frac{11}{32}\right)^2 \text{in.}^2 \times (2.54)^2 \times 9.84 \text{ in.}$$

$$\doteq 5.88 \text{ cm.}^3$$

Then, $$\varepsilon = 1 - \frac{9.220}{5.88 \times 5.12} = 1 - 0.330 = 0.670$$

Surface Area.--See Tables 3 and 6.

$$S_v = \frac{144}{13} \frac{\varepsilon L_2}{1-\varepsilon b} \sqrt{\frac{2RT}{\pi M}} \frac{cm.^2}{cm.^3} \qquad (9)$$

The radical is evaluated as:

$$\sqrt{2 \times \frac{1.987 \text{ cal.}}{\text{gm.mole } ^\circ K.} \times T^\circ K. \times \frac{1}{\pi} \times \frac{1}{\frac{28.0 gm.}{gm.mole}} \times \frac{1000 \text{ gm.-M.}}{2.343 \text{ cal.}} \times \frac{9.80 M.}{sec.^2}}$$

$$\sqrt{188.5\ T}\ \frac{M.}{sec.}$$

Then, $S_v = 152 \sqrt{T}\ \frac{M.}{sec.} \frac{\varepsilon}{1-\varepsilon} \times \frac{L\ sec.}{b^2 cm.^2} \times \frac{M.}{100\ cm.}$

$$S_w = \frac{S_v}{\rho_p} = 1.52 \sqrt{T}\ \frac{\varepsilon}{1-\varepsilon} \times \frac{L_2}{b}\ \frac{M.^2}{cm.^3} \times \frac{1}{\rho_p \frac{gm.}{cm.^3}}$$

Taking an average T of 304°K. and an average L of 52 seconds minus the inherent lag of 2 seconds:

$$S_w = 1.52\ \sqrt{304} \times \frac{0.670}{1-0.670} \times \frac{50}{9.84^2} \times \frac{1}{5.12}\ \frac{M.^2}{gm.}$$

$$S_w = 5.45\ \frac{M.^2}{gm.}$$

Capillary Radius.--See Table 6.

$$r = \frac{2\varepsilon}{1-\varepsilon} \frac{1}{S_w} \frac{1}{\rho_p} \qquad (25)$$

$$r = 2x \frac{0.670}{1-0.670} \frac{1}{5.67 \frac{M.^2}{gm.}} \frac{1}{5.12 \frac{gm.}{cm.^3}} \frac{M.^2}{10{,}000\ cm.^2} \frac{10{,}000 \text{ microns}}{cm.}$$

$r = 0.15$ microns

Ratio of Mean Free Path to Capillary Diameter.--See Table 7.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} \tag{26}$$

Where $\pi\sigma^2$ = effective molecular cross section.

n = number of collisions on the walls of the enclosing vessel per second.

At low pressures the perfect gas law applies so that

$$n = \frac{PV}{RT} \tag{27}$$

Then,

$$\frac{\lambda_1}{\lambda_2} = \frac{P_1}{P_2} \frac{T_2}{T_1} \tag{28}$$

At 75 cm. mercury and 20°C. the mean free path of nitrogen is 0.082 microns.[1] Assuming an average temperature of 30°C. for the present runs:

$$\lambda_2 = 0.082 \text{ microns} \times \frac{75 \text{ cm.}}{P_2 \text{microns}} \times \frac{10^4 \text{microns}}{\text{cm.}} \times \frac{293}{303} \frac{°K.}{K.}$$

$$\lambda = \frac{5.93 \times 10^4 \text{ microns}}{P}$$

---

[1] Handbook of Chemistry and Physics, op. cit., 3088.

Where P is the pressure in microns mercury.

$$M.F.P._1 = \frac{5.93 \times 10^4}{13 \times 1000} = 4.6 \text{ microns}$$

$$\frac{M.F.P._1}{d_c} = \frac{M.F.P._1}{2r} = \frac{4.6}{2 \times 0.146} = 15.7$$

Particle Diameter.--See Table 2. By assuming spheres the equivalent particle diameter is calculated using:

$$S_v = \frac{4\pi\left(\frac{d}{2}\right)^2}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3} = \frac{6}{d} \qquad (29)$$

or, $$d = \frac{6}{S_w \rho} \qquad (30)$$

$$d = \frac{6}{5.67 \frac{M.^2}{gm.} \times 5.12 \frac{gm}{cm.^3}} \times \frac{M.}{10{,}000 cm.^2} \times \frac{10{,}000 microns}{cm.}$$

$$d = 0.26 \text{ microns}$$

If a suitable average particle diameter is already known the surface area may be calculated in a similar fashion. For example, the 28 micron diameter glass beads may be taken:

$$S_w = \frac{6}{d\rho} = \frac{6}{28 \times 2.44} = 0.088 \frac{M.^2}{gm.}$$

APPENDIX III

EXPERIMENTAL DATA

Tables 4 and 5 include the experimental data obtained in these tests. With the exception of the two typical plots, Figures 7 and 8, pressure-time data has not been included directly. Instead the time lags obtained are listed for each run. The value of L used in the calculations is the average time lag for a given run minus the inherent time lag of two seconds. This inherent lag is the measured lag due to the resistance of the filter paper and/or lag in the gauge itself.

Table 4. Data for Density Determinations

Material	Flask volume, cm. 3	Weight of Powder, gm.	Weight of Water, gm.	Temper-ture of Water, °C.	Powder density, gm./cm3
Glass Beads	23.4075	10.1890	19.1648	30.2	2.45
Glass Beads	23.4075	6.4495	20.6726	30.0	2.44
Glass Beads	23.3115	4.9955	21.1711	30.8	2.44
Silicon Carbide	23.4075	3.2456	22.2845	30.0	3.16

Apparently all sizes of the beads manufactured by Minnesota Mining Co., were made of the same type glass. The 28 and 70 micron sizes had the same density within limits of experimental error. Only one run was made of the silicon

carbide since it checked the handbook value of 3.17.

Table 5. Experimental Data for Surface Area and Capillary Radius Calculations.

Run	Material	Weight of Packed Bed, gm.	Length of Packed Bed, cm.	Temperature, °C	Pressure at Bed Inlet, mm. Mercury	Time Lag, Seconds
1a	70 Micron Glass Beads	9.8641	11.15	30.4	11	5
1b				30.0	7	5
1c				30.0	5	6
2a	36 Micron Glass Beads	9.1072	11.05	32.0	9	8
2b				33.0	4	8
2c				33.2	5	11
2d						11
3a	28 Micron Glass Beads	9.5755	10.74	33.3	7	15
3b				33.0	7	13
3c				30.0	6	18
3d				32.0	5	15
4a	Silicon Carbide	9.383	11.0	32.0	14	10
4b				30.6	25	10
4c				29.0	34	10
5a	Aluminum Oxide	4.1037	10.32	33.4	17	8
5b				32.0	20	10
5c				32.0	14	12

Table 5. (Continued) Experimental Data for Surface Area and Capillary Radius Calculations

Run	Material	Weight of Packed Bed, gm.	Length of Packed Bed, cm.	Temperature, °C	Pressure at Bed Inlet, mm. Mercury	Time Lag, Seconds
6a	Iron Oxide	11.8566	10.70	32.0	17	74
6b				29.5	38	73
6c				29.8	19	55
6d				30.2	13	72
7a	Iron Oxide	9.9220	9.84	34.0	13	46
7b				28.0	17	50
7c				30.0	28	50
7d				30.0	27	58
7e				31.0	22	58
8a	Kaolin	2.1095	7.47	32.8	14	56
8b				33.0	10	52
8c				33.0	16	60
8d				33.0	85	53
9a	Silicon Dioxide I	1.1178	4.54	29.8	25	27
9b				29.5	16	25
9c				29.5	14	25
9d				30.0	12	25
9e				30.0	24	24
10a	Silicon Dioxide I	2.1029	8.19	28.5	21	66
10b				28.0	21	72
10c				27.3	30	63

Table 5. (Continued) Experimental Data for Surface Area and Capillary Radius Calculations.

Run	Material	Weight of Packed Bed, gm.	Length of Packed Bed, cm.	Temperature, °C	Pressure at Bed Inlet, mm. Mercury	Time Lag, Seconds
11a	Silicon Dioxide II	0.8834	4.47	32.2	24	13
11b				32.2	11	22
11c				32.0	16	18
11d				30.8	13.5	17
12a	Clay I	1.9037	4.89	30.2	18	35
12b				30.4	30	35
12c				30.4	35	32
13a	Clay II	6.0372	10.14	30.0	30	72
13b				30.0	37	68
13c				30.0	44	63
13d				31.0	31	63
14a	Cupric Oxide	6.7098	10.07	31.0	13.5	12
14b				21.0	9	11
14c				31.3	6	13
14d				31.6	6	15

APPENDIX IV

CALCULATED DATA

Table 6 contains the calculated values of porosities, surface areas and pore radii. Table 7 lists ratios of mean free path to capillary diameter. The M.F.P. indicated as the one for the bed was calculated for the highest pressure at x = b during the run. The M. F. P. at the bed inlet was based on a pressure used in the high pressure tank for one of the runs of a given sample.

Table 6. Calculated Data for Surface Area Determinations

Run No.	Material	Porosity	Surface Area, $M.^2/Gm.$	Pore Radius, Microns
1	70 micron Glass Beads	0.394	0.19	2.9
2	36 micron Glass Beads	0.435	0.57	1.1
3	28 micron Glass Beads	0.399	0.80	0.68
4	Silicon Carbide	0.550	0.68	1.0
5	Aluminum Oxide	0.832	2.55	0.97
6	Iron Oxide	0.638	5.34	0.13
7	Iron Oxide	0.670	5.45	0.15
8	Kaolin	0.818	43.8	0.08
9	Silicon Dioxide I	0.808	56.7	0.07
10	Silicon Dioxide I	0.804	47.8	0.08
11	Silicon Dioxide II	0.851	55.2	0.10
12	Clay I	0.809	56.3	0.06
13	Clay II	0.614	10.1	0.17
14	Cupric Oxide	0.826	2.12	0.70

Table 7. Ratios of Mean Free Path to Capillary Diameter

Run No.	d_c, microns	P_1, mm.Hg	P_2, microns Hg	M.F.P.$_1$, microns	M.F.P.$_2$, microns	$\frac{\text{M.F.P.}_1}{d_c}$	$\frac{\text{M.F.P.}_2}{d_c}$
1	5.7	5	170	11.8	350	2.1	61
2	2.2	5	160	11.8	370	5.4	168
3	1.4	5	70	11.8	850	8.7	625
4	2.1	14	170	4.2	350	2.0	167
5	1.9	14	160	4.2	370	2.1	190
6	0.26	13	40	4.6	1480	17.8	5740
7	0.29	13	60	4.6	990	15.7	3390
8	0.16	10	40	5.9	1480	37.3	9360
9	0.13	12	70	4.9	850	36.6	6340
10	0.16	21	70	2.8	850	17.7	5380
11	0.19	11	140	5.4	420	28.4	2230
12	0.11	18	100	3.3	590	29.5	5300
13	0.33	30	70	2.0	850	6.1	2580
14	1.4	6	160	9.9	370	7.1	265

BIBLIOGRAPHY

1. Knudsen, M., Annelen Physik Leipzig, 35, (1911), 389.

2. Davies, Trefor, editor, Chemical Engineering Practice, New York: Academic Press, Inc. (1956) 2, "Solid State."

3. Barrer, R.M. and Grove, D.M., "Flow of Gases and Vapors in a Porous Medium and Its Bearing on Adsorption Problems," Part II, "Transient State," Transactions of the Faraday Society, 47, (1951) 826-844.

4. Arnell, J.C., "Permeability Studies, II. Surface Area Measurements of Inorganic Paint Powders," Canadian Journal of Research, 25, Section A, (1947), 191.

5. Barrer, R.M., Diffusion in and Through Solids, New York: The Macmillan Co., (1941).

6. Barrer, R.M., "A New Approach to Gas Flow in Capillary Systems," Journal of Physical Chemistry 57, (1953) 35-40.

7. Carman, P.C., Flow of Gases Through Porous Media, New York: Academic Press, Inc., (1956).

8. DallaValle, J.M., Notes on Diffusion, Unpublished notes accumulated by the author, (1951).

9. Patterson, G.N., Molecular Flow of Gases, New York: John Wiley & Sons, Inc., (1956), 159-163.

10. Kraus, Gerard; Ross, J.W.; Girifalco, L.A., "A Study of Porous Media by Means of Flow Methods," Technical Report I, Applied Science Research Laboratory, University of Cincinnati, July 29, 1952.

11. Carman, P.C., and Raal, F.A., "Kinetics of Sorption by Porous Solids," Transactions of the Faraday Society 50, (1954), 842.

12. Knudsen, Martin, The Kinetic Theory of Gases, New York: John Wiley & Sons, Inc., 3rd ed., (1950).

13. Ruby, W.R. and Loveland, R.P., "Determination of the Density of a Fine Powder," Journal of Physical Chemistry 50, (1946), 345.

14. DallaValle, J.M., Micromeritics, New York: Pitman Publishing Corp., 2nd ed., (1948).

15. Jost, W., Diffusion in Solids, Liquids, Gases, New York: Academic Press, Inc., (1952).